

Growth and characterization of single crystal Ga_2O_3 nanowires and nano-ribbons for sensing applications.

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ABSTRACT

The growth of monoclinic Ga_2O_3 nanowires, nano-ribbons and nano-sheets has been investigated. Results indicate that high quality single crystal nanowires can be grown at 900°C using an Au catalyst, while single crystal nano-ribbons and nano-sheets require no metal catalyst for growth. Since bulk Ga_2O_3 is a promising material for high temperature sensing, Ga_2O_3 nanowires and nano-ribbons may prove to enhance the sensing capability due to the high surface area. We have investigated the nature of defects in this material using Electron Spin Resonance, in as grown material, as well as under annealing in a reducing gas (H_2) at various high temperatures. Results indicate the presence of an oxygen deficiency in the material, resulting in a conduction electron signal that becomes enhanced with annealing. An alternate use of these nanowires for sensing applications will also be presented, involving Surface Enhanced Raman Spectroscopy.

1. INTRODUCTION

One-dimensional structures, such as carbon nanotubes and semiconductor nanowires, are currently of great interest due to their unique physical properties and potential applications.¹⁻³ A number of applications have been investigated for such 1D structures, including nanoscale devices^{4,5} and sensor applications.⁶ Bulk monoclinic gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) is a wide band gap semiconductor ($E_g = 4.9$ eV), which exhibits conduction and luminescence properties^{7,8}, with applications to opto-electronics and high temperature gas sensing.⁹⁻¹³ Recently, several groups have reported the growth of $\beta\text{-Ga}_2\text{O}_3$ nanowires by various techniques¹⁴⁻¹⁷, using the vapor liquid solid (VLS) mechanism, with either Au, Ni or oxygen as a catalyst. Since this material (in bulk or thin film) shows promise for high temperature gas sensing, it is important to examine the possible sensor-related properties of Ga_2O_3 nanowires, which have a very large surface to volume ratio and thus may result in higher sensitivity devices.

In this manuscript, we will present results on the growth of $\beta\text{-Ga}_2\text{O}_3$ nanowires and examine their optical and structural properties. We will also address two possible sensor-type applications of such wires, including high temperature gas sensing, as well as the use of these wires as substrates for surface enhanced Raman spectroscopy (SERS).

2. EXPERIMENTAL PROCEDURE

Elemental Ga of 99.995% purity was used as the starting material. The substrate material used included Si(100) and Si(111), and GaAs (100) substrates, which were first ultrasonically cleaned by placing each sample in acetone and then in methanol for a duration of five minutes. Following the cleaning procedure, the samples were dried using N_2 gas. After the cleaning process, some of the Si samples were covered with a 20nm Au film, which was deposited in vacuum using an electron beam. The GaAs substrates were covered with a 10nm Ni layer and some were left uncoated, and used as a source material in several growths. The source material (either GaAs or pure Ga metal) was then placed at one end of a 4" alumina boat, with the substrate at the opposite end. The boat was then inserted into a

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quartz tube inside a tube furnace, which was evacuated to a base vacuum of 40 mTorr using a mechanical pump. The furnace was then heated to temperatures between 700°C and 1000°C. Several gas feed valves and flow controllers were connected to the other end of the tube, allowing a controlled flow of argon and oxygen gas to pass over the alumina boat. During the heat up cycle, the evacuated quartz tube was flushed several times with argon gas in order to reduce the initial oxygen content. Once at temperature, the growth was initiated by the flow of a 6:1 ratio of argon to oxygen. The quartz tube pressure remained generally in the 6 Torr range while flowing the Ar/O₂ gas mixture. The wire growth was studied as a function temperature, sample position, choice of substrate/catalyst, and source material. As-grown nano-ribbons and nanowires were examined for structural and composition using a Leica Cambridge Stereoscan 360FE scanning electron microscope (SEM) with EDX capabilities, a Hitachi High Resolution Transmission Electron Microscope (HRTEM), and Raman spectroscopy. Since bulk Ga₂O₃ has found application in high temperature sensing of reactive gasses such as hydrogen, the evolution of defects for as grown material and material annealed in a hydrogen atmosphere was also studied using electron spin resonance (EPR). This was done in order to determine the effects that high surface area nanostructures may have on the sensing capabilities of this system. In addition, we have found that the resultant Ga₂O₃ nanowires also exhibit promising properties as substrate material for surface enhanced Raman (SERS). The SERS spectra for Rhodamine 6G were obtained using a μ Raman system, which consisted of a Mitutoyo Microscope and a SPEX Triplemate spectrometer equipped with a CCD. The 514.5 nm line of an Ar ion laser was used as the excitation source. The microscope had 10X, 50X and 100X objectives for focusing the laser light and was coupled to the spectrometer through a fiber optic bundle. The light from the microscope, was filtered by a 514.5 nm notch filter. The positions of the Raman lines in a given spectrum were calibrated against the 546.0 nm emission line from a fluorescent light source

3. GALIUM OXIDE NANOWIRE GROWTH

Under the experimental conditions described above, it was found that no nanowire growth occurred without the presence of a metal catalyst layer. Once this was determined, two different substrate/catalyst structures were examined for growth of nanowires with mixed success. The first system investigated involve the use of a 10nm nickel catalyst layer on GaAs(100) substrate, using both a GaAs wafer and elemental Ga as the source material. Although some success was realized using these materials, we found that the use of a 20nm Au catalyst on Si, combined with a solid Ga source, resulted in the best nanowire and nano-ribbon material, as will be discussed in the following section.

3.1 Growth of nanowires using GaAs substrate and Ni catalyst.

The first set of growths involved the use of Ni:GaAs substrates and a GaAs source material. In general, no growth was noted for temperatures below 750°C or above 900°C. A representative example of nanowire growth at 800°C is shown

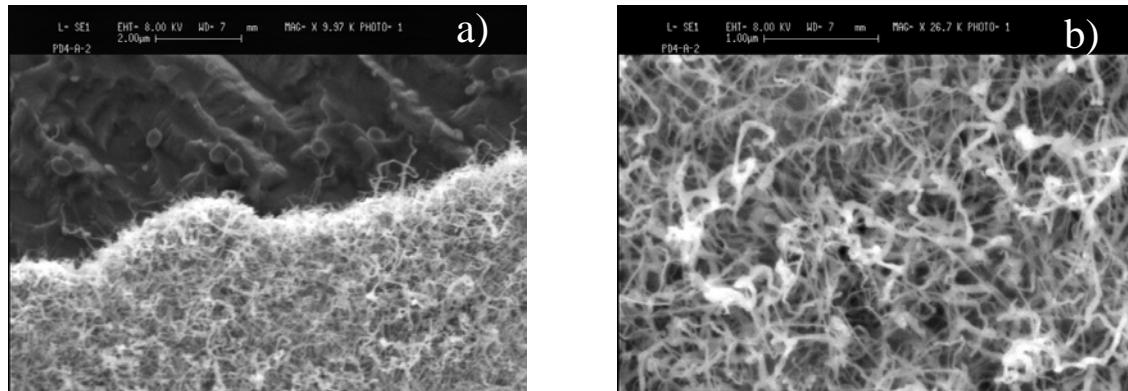


Fig. 1 SEM image of nanowire blanket grown on GaAs at 800 °C using a 10nm film of Ni as a catalyst and GaAs as a vapor source.

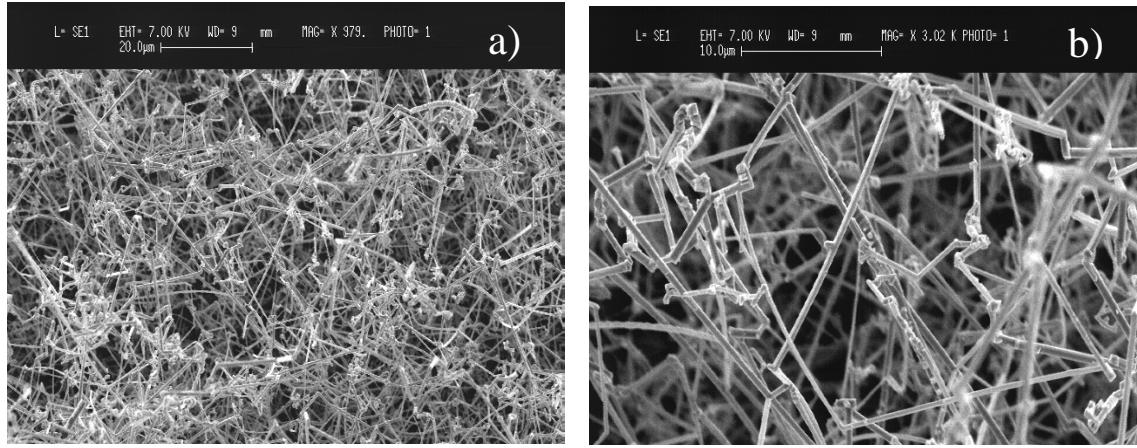


Figure 2. An SEM image of the nanowires which were grown at 800 °C using solid Ga as the vapor source.

in Figure 1 a,b. As can be seen, a thick nanowire film forms on top of the existing GaAs sample, as shown in Fig. 1a. However, the nanowires are very non-uniform and bent, as shown in Fig. 1b. The EDS analysis determined that they consist of a 1:1 ratio of Ga and O and no Raman signal for Ga_2O_3 (stable β -gallium oxide) could be found. In addition, TEM investigations have shown the wires to be amorphous. Since the nanowires exhibited very curved structures and lower Ga content, it was thought that the Ga flux was not sufficient from the GaAs source sample, leading to a very slow growth process with reduced Ga content. Thus, a solid Ga source was substituted for the GaAs. The results are shown in Figure 2a,b. As can be seen, a high density of nanowires was formed, which now have a straighter growth morphology, as shown in Fig. 2a. Upon closer examination, however, the wires have many kinks and bends, and they are extremely large, with a diameter on the order of 0.7 μm , as shown in Fig. 2b. However, EDS analysis suggested that the wires consisted of Ga_2O_3 .

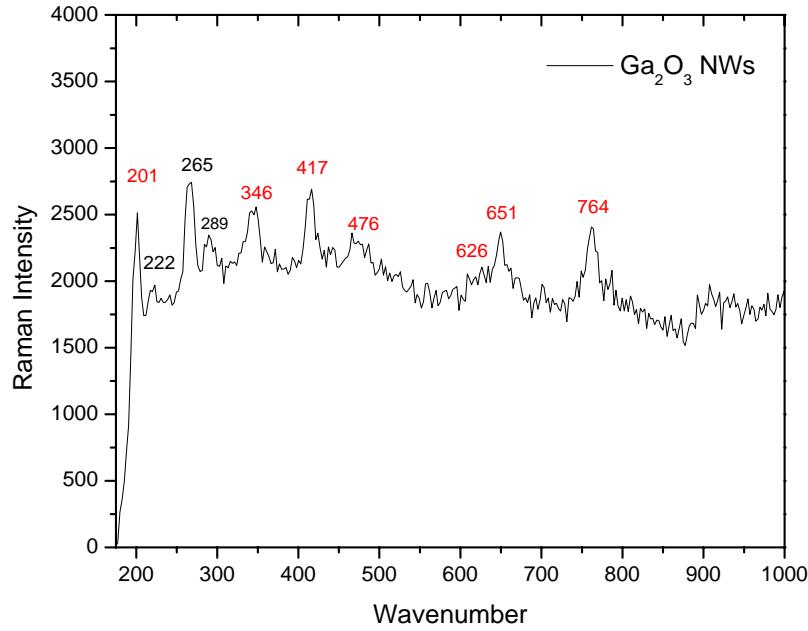


Fig3. Raman spectrum, of the nanowires shown in Fig. 2, corresponding to monoclinic Ga_2O_3 .

In order to fully establish the structural and chemical composition of these wires, Raman spectroscopy was used. The Raman spectrum for the nanowires in Figure 2 is shown in Figure 3. The Raman lines for bulk β -Ga₂O₃ are at 198, 346, 416, 476, 630, 653 and 766 cm⁻¹ and have been reported by Sulikowski et al.¹⁸ and Zhang et al.¹⁷. The bands between 300-600 cm⁻¹ correspond to bending vibrations while those above 600 cm⁻¹ are due to Ga-O₄ tetrahedral stretching¹⁸. A comparison between the lines for bulk β -Ga₂O₃ and those of the nanowires shown in Figure 3 confirms that the nanowires consist of stoichiometric monoclinic Ga₂O₃. The lines at 222, 265 and 289 cm⁻¹ (shown in black) are from the underlying GaAs substrate¹⁹.

3.2 Growth of nanowires using solid source Ga and Au catalyst.

Although it was possible to grow nanowires using a GaAs substrate with a Ni catalyst, the wire morphology could not be fully optimized. However, better results were obtained using Au as a catalyst on a Si substrate, with a solid Ga source. A temperature range between 700°C and 1000°C was investigated, with results showing no nanowire growth below 775°C or above 900°C. The optimal growth conditions were between 800°C and 900°C, at a 6:1 argon to oxygen gas ratio. An example of the wires grown under optimal conditions is shown in Figure 4 a,b. As can be seen, the wires

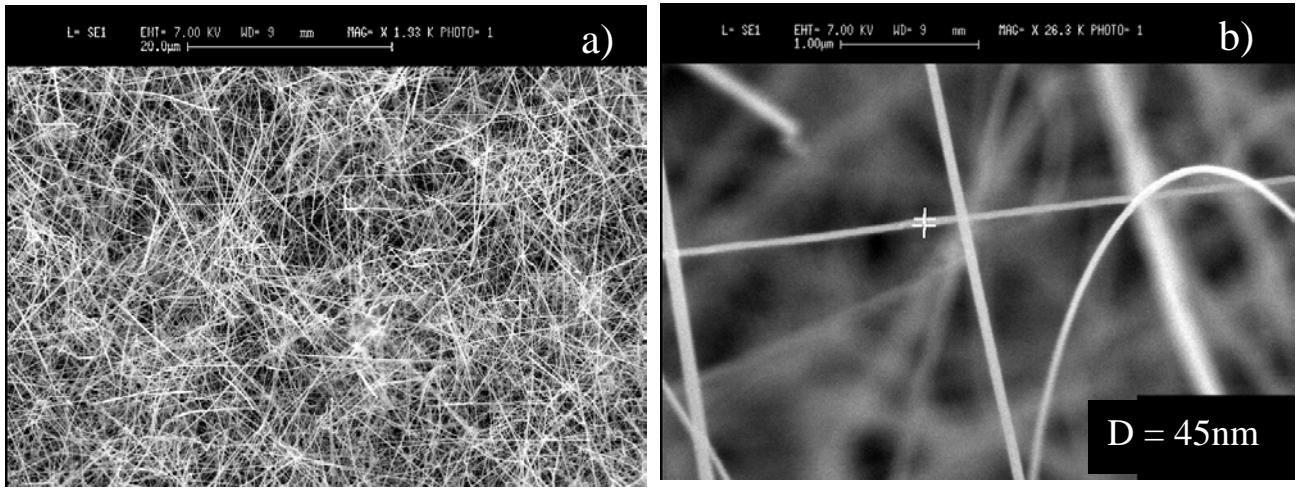


Figure 4. SEM images of monoclinic Ga₂O₃ nanowires grown at 900°C, using an Au catalyst and a Si substrate.

are very straight, with no noticeable growth anomalies. In addition, the nanowires are significantly narrower, with an average diameter of 40 – 50 nm. Lengths as long as 50 μ m have been observed for longer growth times. The Raman spectroscopy analysis indicates that the wires consist of monoclinic Ga₂O₃, which is an optimal structure for high temperature sensing applications. The Raman spectrum is very similar to that shown in Figure 3, but the Raman lines associated with the GaAs substrate are missing, and the Si substrate line at 521 cm⁻¹ is present instead, as would be expected.

The crystallinity of these nanowires has also been examined, and a high resolution TEM image of a single wire, along with the diffraction image, is shown in Figure 5. The single crystal nature of the nanowires can be determined from both the lattice fringes as well as the diffraction image. Some stacking faults are also evident along the wire length, which are also evident from the diffraction pattern.

The monoclinic Ga₂O₃ nanowires also exhibit an intense blue luminescence, near 475 nm, as has been reported by other groups¹⁶. The emission in the blue region has been attributed to the presence of oxygen vacancies²⁰. In fact, Binet and Gourier²¹ have suggested that this blue PL is produced by the recombination of an electron on an oxygen donor vacancy with a hole on an acceptor (such as a Ga vacancy). Interestingly, this 475nm emission has been reported only in nanowires that have been produced using Au as a catalyst¹⁵. The nanowires, which have been grown using a Ni catalyst, exhibit a PL which is more blue shifted toward the UV¹⁶.

The importance of the metal catalyst has also been investigated. In fact, no nanowire growth was obtained without a metal catalyst under the conditions described above, no matter whether GaAs or Si was used as a substrate.

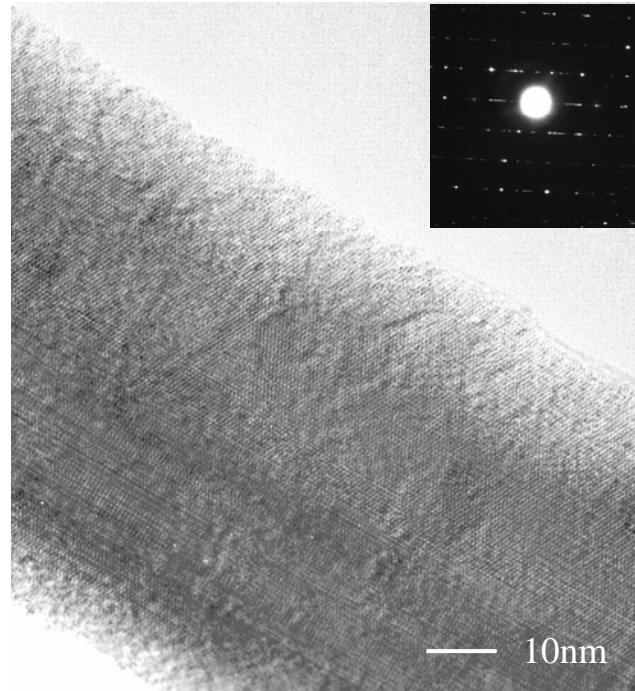


Figure 5. HRTEM and associated diffraction image of Ga_2O_2 nanowires Ga_2O_3 grown at 900°C, showing lattice fringes.

Thus, the metal catalyst, which forms a liquid eutectic with the Ga vapor, is critical, suggesting the growth process follows the well known vapor-liquid-solid (VLS) growth mechanism²². This is further supported by the fact the tip of the nanowires consists of this eutectic alloy drop, as would be expected in the VLS mechanism.

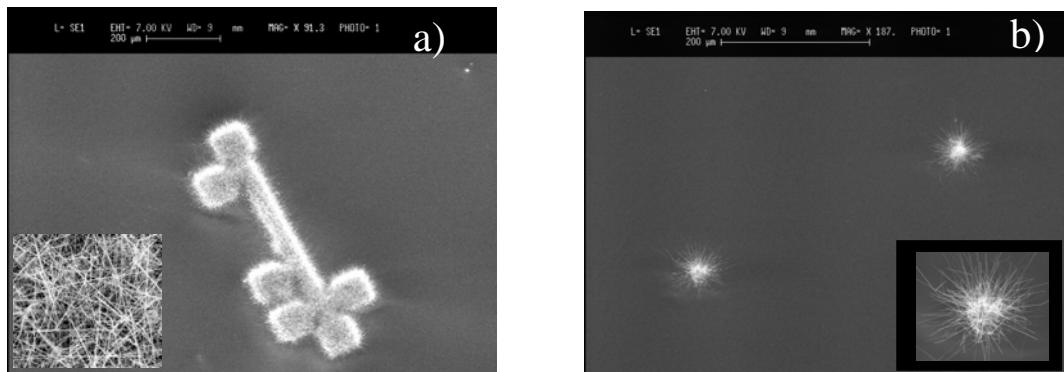


Figure 6. Nanowire growth using photolithographically produced Au catalyst patterns.

Since in our case, the presence of the metal catalyst is critical for nanowire growth, it is easy to develop a number of patterns for the growth of nanowires for specific device applications. An example of the structures, which can be grown with Ga_2O_3 nanowires using a lithographically defined Au pattern, is shown in Figure 6a,b. In this case,

the specific pattern in Fig. 6a has been designed in order to allow the measure of nanowire mobilities. Inset images in the figure show a higher resolution image of the nanowires within these patterned regions.

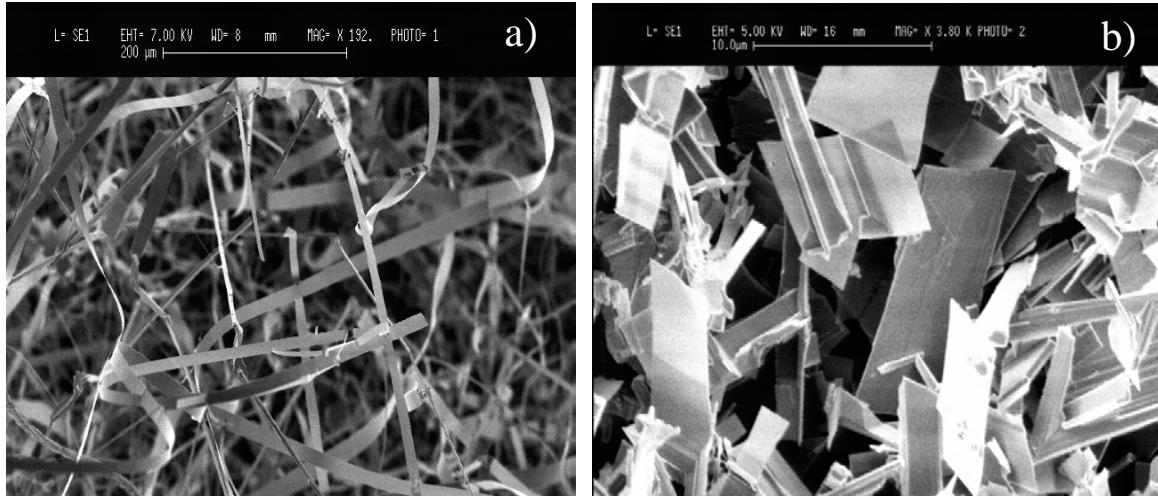


Figure 7. Ga_2O_3 nano-ribbons (a) and nano-sheets (b) formed at 900 °C directly on metal Ga surface.

As we have shown, the Ni or Au metal catalyst is necessary for successful nanowire growth on the Si, GaAs or other substrate. We have also found that Ga metal itself can act as a catalyst directly, but in this case, only Ga_2O_3 nano-ribbons and nano-sheets can be formed. This growth process occurs directly on the Ga metal source material, when the temperature is between 800 and 850°C, with a 6:1 argon to oxygen gas ratio. An example of the nano-ribbons and nano-sheets, which can be formed in gram quantities, is shown in Figure 7a,b. As can be seen, the nano-ribbons are generally on the order of 10 or 15 μm wide, only 10s of nanometers thick, and longer than 300 μm , while the nano-sheets are generally 5-10 μm on a side, and as thick as the nano-ribbons.

4. SENSOR-RELATED PROPERTIES OF Ga_2O_3 NANO-RIBBONS AND NANOWIRES

In general, nanowires or nano-ribbons are 2D structures with very small diameters, and thus they consist of a very high surface/volume ratio. This may prove beneficial when used in certain types of sensor applications, such as those which take advantage of surfaces and electrical properties, as well as others, which may take advantages of the nanowire size as well as the capability of nanowire manipulation.

4.1 Defect-related properties of Ga_2O_3 nano-ribbons as a function H_2 anneals: Application to high temperature sensing.

It has been reported previously that polycrystalline thin films of Ga_2O_3 are quite effective as a base material for high temperature sensing of oxygen²³, reducing gases^{23,24}, as well as for hydrocarbons²⁵. The important feature of this material is the high temperature stability and thermal stability (melting T is near 1900°C). Since this material is n-type, due to the presence of oxygen vacancies, it is an ideal material to use in sensors that are based on the changes in the electrical properties. In the case of oxygen sensing, Ga_2O_3 polycrystalline thin films have been used in the temperature range of 900-1000°C, taking advantage of bulk effects²⁶. At lower temperatures (<700°C), the Ga_2O_3 thin films have been studied for reducing gas sensing, mainly taking advantage of surface effects^{27,28}. In fact, at 600°C, a significant resistance lowering effect has been noted for such sensors when subjected to a 1% H_2 gas in atmosphere²⁷. In view of these results and the fact that Ga_2O_3 nanowires and nano-ribbons consist mostly of surfaces, it is important to investigate the behavior of the defect states associated with the oxygen vacancy (which leads to the electrical behavior) at higher temperatures and as a function of H_2 gas.

In order to investigate this, Ga_2O_3 nano-ribbons were produced as discussed above, and electron spin resonance spectroscopy was performed on these nano-ribbons after a number of anneals in 5% H_2 and Ar gas mixture. The reason for the use of the nano-ribbons is twofold. First, gram quantities of this material could be produced, allowing sufficient material for the EPR studies, and secondly, the nano-ribbons exhibit high surface areas with flat and uniform surfaces, which should allow easier interpretation of the results. The EPR results for the fresh sample, at room temperature, and at various measurement temperatures is shown in Figure 8 a,b. The resonance, shown in Figure 8a is quite sharp,

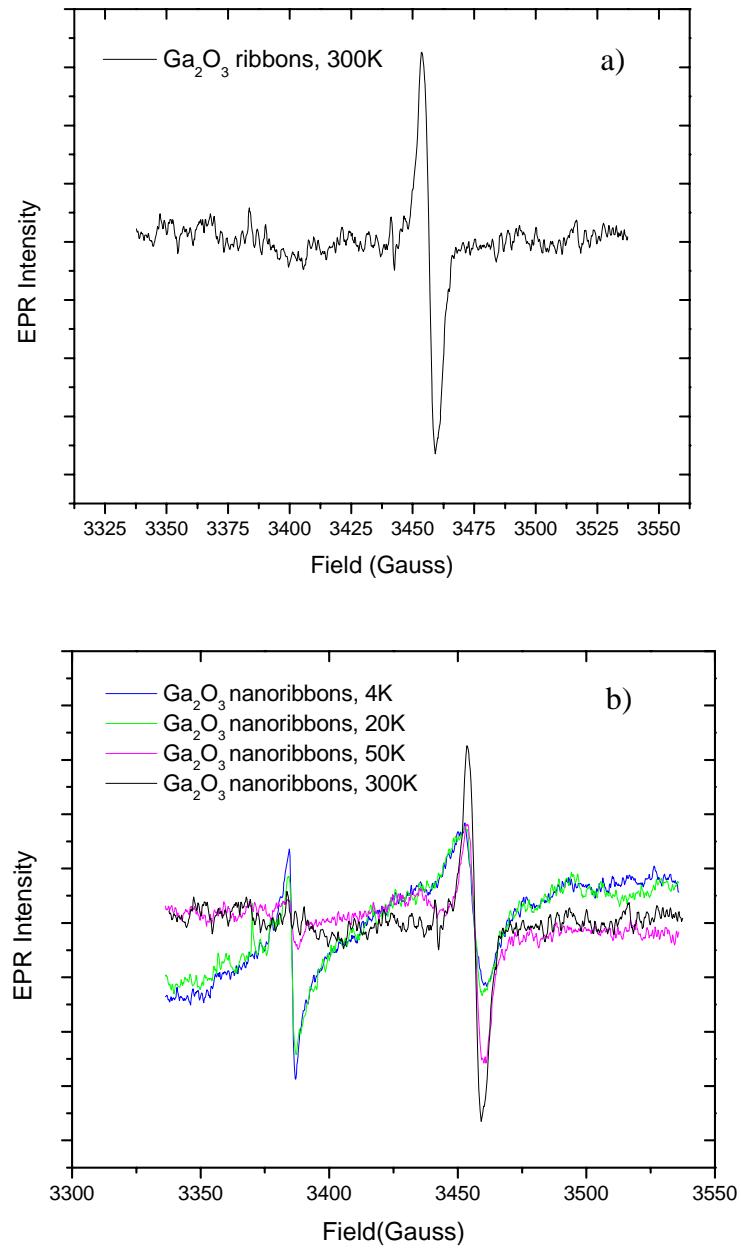


Figure 8. EPR spectrum of the nano-ribbons at 300K, (a) and as a function of measurement temperature (b).

with a g value of 1.961, which is similar that reported by Binet and Gourier²¹ in the case of single crystal Ga_2O_3 . Since this resonance does not show a marked dependence on the measurement temperature, as seen in Fig. 8b, one can conclude that it is due to de-localized conduction electrons, which originate from the oxygen vacancy site. This is in agreement with the results of Binet et al.²¹

It is these de-localized electrons which result in the n-doping in the existing material, and thus, it is important to examine the stability of this resonance (and thus these conduction electrons) with higher temperature reducing gas anneals. Since the gas sensors discussed above are generally based on the electrical properties of the Ga_2O_3 material, any changes of the de-localized electron signal can directly affect the sensitivity of such devices. Thus, experiments have been carried out in which the nano-ribbons have been subjected to various temperatures anneals in a H_2/Ar atmosphere, and the resonance at $g = 1.961$ has been measured after each treatment. Results are shown in Figure 9.

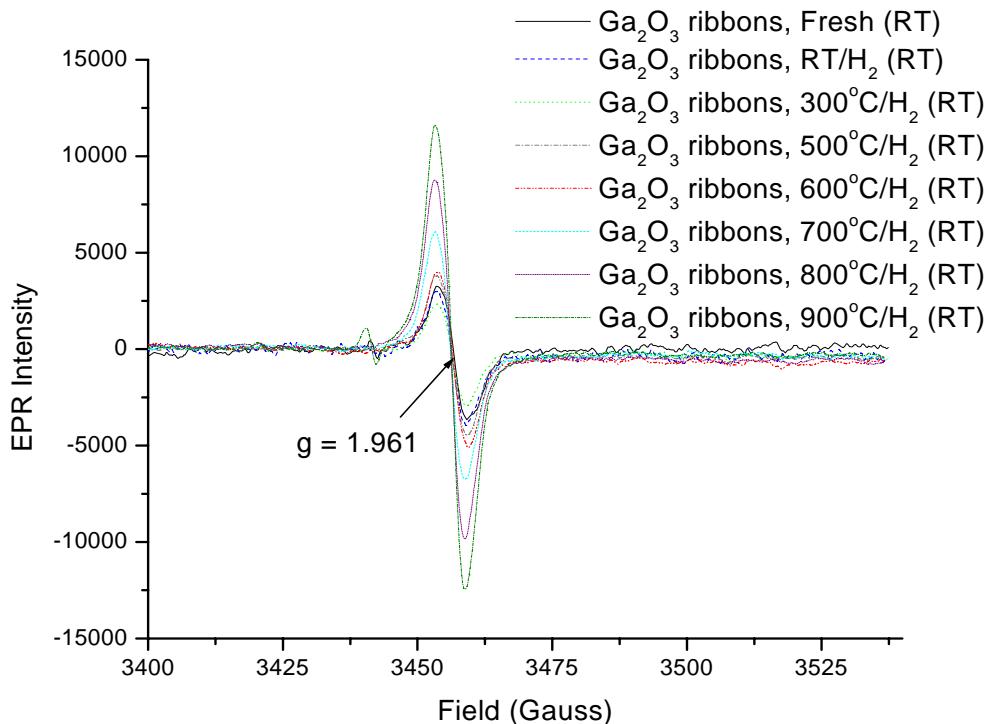


Figure 9. EPR spectra for the Ga_2O_3 nano-ribbons subjected to H_2/Ar atmosphere anneal at temperatures shown.

As can be seen, although the signal intensity drops slightly in the first anneal at 300°C, further anneals in H_2 at higher temperatures result in continuous increases in the conduction electron signal, and at 900°C, the conduction electron signal increased by a factor of 4. Further anneals at higher temperatures lead to a significant drop of the signal strength, most likely due to structural changes of the nano-ribbons. The significant increase of the signal at 900°C suggests that a sensor based on the conductivity in these nano-ribbons may indeed exhibit enhanced sensitivity in the high temperature regime.

4.2 Optical properties of Ga_2O_3 nanowire/metal composites and application to Surface Enhanced Raman (SERS).

The detection and manipulation of very small numbers of molecules in liquid or gaseous phases is of interest for both fundamental and applied reasons. One promising technique for sensing involves Raman scattering (RS), which

is an optical probe that can provide a unique fingerprint for the chemical or material being analyzed. In RS, the characteristic vibrational modes of a molecule are detected *via* the inelastic scattering of an incident laser line that occurs when these modes are excited. This allows for unique identification of a molecule and provides information about the molecular bonding involved. However, a key issue for RS is that the cross-sections are very small. Typically, the intensity of a line due to inelastic scattering by a molecular vibration, relative to that of the elastically-scattered (Rayleigh) line, is $\sim 10^{-8}$. Hence, conventional RS is useable mainly for pure or highly concentrated samples having a density of scattering centers of $\sim 10^{22}$ - 10^{23} cm $^{-3}$.

It is well known that Raman scattering can be significantly enhanced for certain chemicals if they adsorb on nanostructured metal surfaces²⁹⁻³¹. As the laser light reaches the nanostructured surface, it excites plasmons in these metal nanostructures, enhancing the local electric fields, which in turn couple with the dipoles of the adsorbed molecule. In addition, the local fields at the surface of the nanostructures are enhanced by the small dimensions involved. All of these effects lead to enhancements of the Raman scattering from the surface-adsorbed molecule by as much as 10^{16} theoretically²⁹⁻³¹ and 10^6 experimentally²⁹⁻³¹. However, the current situation is such that there is no comprehensive model to explain the SERS effect, and thus it very difficult to design SERS-active substrates for a specific molecular species.

In the study of surface enhanced Raman scattering, there is a small group of compounds that are routinely used to evaluate the efficacy of a given SERS substrate. Some of these include Rhodamine 6G, pyridine, benzoic acid and benzene. In order to compare to a standard, we have used Rhodamine 6G (RH6G) for our initial studies. In case of our nanowire SERS substrate design, 40 nm Ga₂O₃ nanowires were produced as discussed above. The nanowires were grown, removed from the substrate by sonication in a methanol solution and then deposited on a clean Si substrate, using a micro-pipette. A 6nm coating of Ag was deposited on the nanowires, forming Ga₂O₃/Ag nanowire composite. Shown in Figure 10 a,b is the SEM image of the solution deposited nanowire composites and the corresponding surface enhanced Raman scattering for 10^{-6} M of Rhodamine 6G dissolved in methanol and applied by exposing the nanowire substrates to a controlled amount of solution.

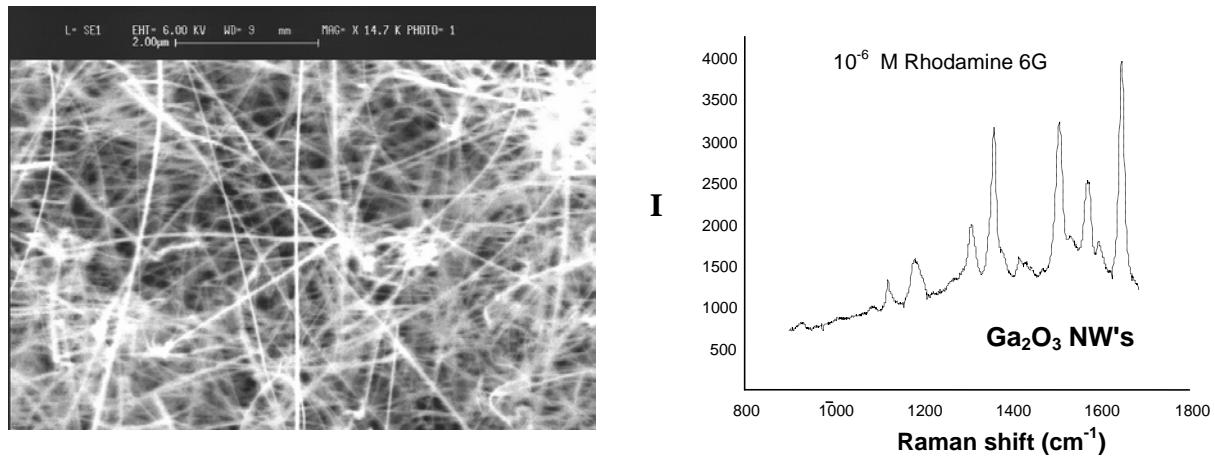


Figure 10. SEM image of Ga₂O₃/Ag nanowires (a) and the corresponding SERS signal for a 10^{-6} M dilution of Rhodamine 6G.

These nanowire composites exhibited the strongest SERS signal from all the SERS substrate we studied, and we could get sensitivity to 10^{-9} M Rhodamine 6G. We believe that the reason for this is the fact that the dielectric/metal composite wires have numerous crossing points, which enhances the chance for “hot” spots to form. These “hot” spots are regions with very high electric fields³², due to close proximity of other nanowires. The Raman signal in these regions is thought to be significantly enhanced due to the large electromagnetic fields present.

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REFERENCES

1. A.M. Morales and C.M. Lieber, *Science* **279** (1998) 208.
2. J.D. Holmes, K.P. Johnston, R.C. Doty and B.A. Korgel, *Science* **287** (2000) 1471.
3. Deyu Li, Yiyi Wu, Philip Kim, Li Shi, Peidong Yang and Arun Majumdar, *Appl. Phys. Lett.* **83** (2003), 2934.
4. Yi Cui, Zhaohui Zhong, deli Wang, Wayne U. Wang and Charles M. Lieber, *Nano Letters* **3** (2003) 149.
5. E.S. Snow, J.P. Novak, P.M. Campbell and D. Park, *Appl. Phys. Lett.* **82** (2003) 2145.
6. Y.X. Liang, Y.J. Chen and T.H. Wang, *Appl. Phys. Lett.* **85** (2004) 666.
7. T. Harwig, J. Schoonman, *J. Solid State Chem.* **23** (1978) 205.
8. W.C. Herbert, H.B. Minnier, J.J. Brown, Jr., *J. Electrochem. Soc* **116** (1969) 1019.
9. D.D. Edwards, T.O. Mason, F. Goutenoir and K.R. Poeppelmeier, *Appl. Phys. Lett.* **70**, (1997) 1706.
10. M. Fleischer, J. Giber and H. Meixner, *Appl. Phys.* **A54** (1992) 560.
11. F. Reti, M. Fleischer, H. Meixner and J. Giber, *Sensors and Actuators* **B18-19** (1994) 138.
12. M. Ogita, N. Saika, Y. Nakanishi and Y. Hatanaka, *Appl. Surf. Science* **142** (1999) 188.
13. J. Zosel, K. Ahlborn, R. Muller, D. Westphal, V. Vashookl and U. Guth, *Solid State Ionics* **169** (2004) 115.
14. X.C. Wu, W.H. Song, W.D. Huang, M.H. Pu, B. Zhao, Y.P. Sun and J.J. Du, *Chem. Phys. Lett.* **328** (2000) 5.
15. C.H. Liang, G.W. Meng, G.Z. Wang, Y.W. Wang, L.D. Zhang and S.Y. Zhang, *Appl. Phys. Lett.* **78** (2001) 3202.
16. H.J. Chun, Y.S. Choi, S.Y. Bae, H.W. Seo, S.J. Hong, J. Park, and H. Yang, *J. Phys. Chem.* **107** (2003) 9042.
17. H.Z. Zhang, Y.C. Kong, Y.Z. Wang, X. Du, Z.G. Bai, J.J. Wang, D.P. Yu, Y. Ding, Q.L. Hangand S.Q. Feng, *Solid State Commun.* **109** (1999) 677.
18. B. Sulikowski, Z. Olejniczak and V. Cortes Corberan, *J. Phys. Chem.* **100**, (1996) 10323.
19. Reference for Raman line of GaAs
20. T. Harwig, F. Kellendonk, *J. Solid State Chem.* **24** (1978) 255
21. L. Binet and D. Gourier, *J. Phys. Chem. Solids* **59** (1998), 1241.
22. R.S. Wagner and W.C. Ellis, *Appl. Phys. Lett.* **4** (1964) 89.
23. M. Ogita, N. Saika, Y. Nakanishi and Y. Hatanaka, *Appl. Surf. Science* **142**, (1999) 188.
24. M. Fleischer, L. Hollbauer and H. Meixner, *Sensors and Actuators* **18-19**, (1994) 119.
25. J. Zosel, K. Ahlborn, R. Muller, D. Westphal, V. Vashook and U. Guth, *Solid State Ionics* **169**, (2004) 115.
26. M. Fleischer and H. Meixner, *Sensors and Actuators* **B5** (1992) 115.
27. M. Fleischer, J. Giber and H. Meixner, *Appl. Phys.* **A54** (1992) 560.
28. M. Fleischer, F. Reti, H. Meixner and J. Giber, *Sensors and Actuators* **B 18-29** (1994) 573.
29. E. Hao and G.C. Schatz, *J. Chem. Phys.* **120**, 357 (2004) 357.
30. M. Kerker, D.S. Wang, and H. Chew, *Appl. Optics*, **19**, (1980) 3373.
31. M. Moskovits, *Rev. Mod. Phys.* **57**, (1985) 783.
32. J.P. Kottmann and O.J.F. Martin, *Optics Express* **8**, (2001) 655.